

METHOD OF CHECKING ADJUSTING THE CONTENT OF CRYSTALLIZATION NUCLEI IN A MELT

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Abstract of **GB1352567**

1352567 Sampling molten metal S L BACKERUD 28 April 1971 11941/71 Heading B3F [Also in Division C7] In order to determine whether a first metal melt has the desired amount of crystallizing nucleants, a sample is taken from the melt by immersing a test vessel, at a temperature higher than the nucleating temperature of the melt, in the melt. The test vessel is withdrawn from the melt and the sample is allowed to solidify under controlled conditions, a record of the sample's temperature being made at various times during its solidification. A cooling curve of temperature against time is plotted. This curve is then compared with a second curve obtained for a second standard melt of the same composition as the sample but having the desired amount of nucleant and solidified under the same controlled conditions as the sample. If the solidification curve of the sample differs from that of the standard, nucleants can be added to the first melt or can be removed therefrom by filtration or decanting. The controlled conditions under which the sample is solidified are:-(i) the convection of the melt is reduced to minimum, e.g. by application of a magnetic field, (ii) heat dissipation from the sample takes place in all directions, (iii) the thermocouple used is placed centrally of the sample, and (iv) the materials of the test vessel, thermocouple &c. do not act as nucleants for the melt. It is also preferable that the sample has a volume of 5- 50 cc. and that the thermocouple is placed not less than 1 cm. from the test vessel wall. Tests on aluminium, aluminium-silicon alloy (both using graphite crucibles as test-vessels) and cast iron (using a ceramic crucible) are exemplified. The effectiveness of primary nucleation in melts can be compared by observing the supercooling necessary before onset of nucleation and the slope of the curve in the "plateau" region where the latent heat of solidification slows down cooling of the melt. For judging the effectiveness of secondary nucleation, e.g. the solidification of Al-Si eutectic in Al-Si alloys, or of nodular graphite in cast iron, the area under positive values of the derivative during recalculation of the sample may be measured.

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(54) A METHOD OF CHECKING AND ADJUSTING THE
CONTENT OF CRYSTALLIZATION NUCLEI IN A MELT

(71) I, STIG LENNART BACKERUD,
of Vollmovägen 3, Akersberga, Sweden, a
Swedish citizen, do hereby declare the inven-
tion, for which I pray that a patent may be
granted to me, and the method by which it
is to be performed, to be particularly de-
scribed in and by the following statement:—

The present invention relates to a method
for checking and controlling the content of
crystallization nuclei in a melt. In principle,
the method can be used in connection with
all crystalline solidification processes, but has
been particularly developed for the purpose of
assessing and regulating the solidification of
metal melts.

The properties of crystalline substances are
mainly dependent on the physical processes
occurring when the material passes from the
liquid to the solid phase. In addition to such
external factors as the construction of the
mould, its heat transferring ability and the
rate of solidification, the size, morphology, dis-
tribution and directionality of the formed
crystals are dependent on the number of active
nuclei, i.e. crystal grains present in the melt
during the solidification process or located on
those surfaces with which the melt comes into
contact.

Normally, the number of active nuclei in
newly manufactured metals is too small to
provide for a homogeneous, fine-grain
crystalline solidification. Consequently, it is
often desired to stimulate nucleation by add-
ing different substances or particles to the melt
or to the casting equipment. The nucleation
effect, however, is dependent on the physical
and chemical condition of both the melt and
the added substances.

An ordinary qualitative and quantitative
chemical analysis of the melt, including the
additives, will not therefore provide positive
information on the actual nucleation effect
attained during the solidification process, since
the physical and chemical state of the melt
does not only depend on the concentration of
the different components. Consequently, when
casting metallic materials it is normal practice

to cast first a sample which after cooling is
cut and prepared for examination, whereafter
the obtained structure is studied by
metallographical methods. This procedure,
however, is time consuming and unavoidably
reduces the production rate. Moreover, the
properties of the melt can change during the
time taken to carry out tests, whereby the
obtained result is no longer valid when the
metal is cast.

With other casting methods, nucleation is
suppressed instead of stimulated. Also in this
instance, the inherent nucleation tendency of
the melt is examined, by casting sample
ingots.

By intensively studying the thermal condi-
tions prevailing during nucleation and crystal
growth, a method has been developed where-
by the nucleation ability of a metal melt can
be established from a sample taken from the
melt within the course of a few minutes,
whereafter, if necessary, the nucleation ability
of the melt can be corrected by adjusting the
content of crystallization nuclei in the melt.
This applies to both primary and secondary
nucleation, i.e. both the first solid phase
formed from the melt and the elements or
intermediary phase separated during the pro-
cess of solidification.

The present invention provides a method of
checking and adjusting the content of
crystallization nuclei in a first melt, compris-
ing;

- (a) taking a sample from the melt by
immersing a test vessel in the melt;
- (b) removing the test vessel from the melt;
- (c) permitting the sample to solidify in
the test vessel under certain conditions
specified below;
- (d) measuring the temperature of the sample
at various times during the solidification of
the sample;
- (e) obtaining a first solidification curve by
plotting a graph of temperature of the sample
against time;
- (f) comparing at least one of the following
characteristics of the curve: the slope of the

primary plateau temperature and the areas under positive values of the derivative of the curve with the corresponding characteristic(s) of a second solidification curve obtained by (i) measuring the temperature of a second melt at various times during solidification under said certain conditions, the second melt having the same composition as the first melt but having a desired content of crystallization nuclei and (ii) plotting a graph of the temperature of the melt against time; and

(g) adjusting the content of crystallization nuclei in said first melt if said compared characteristics differ substantially to make the content of crystallization nuclei in said first melt substantially equal to said desired content.

Thermal analysis for determining the chemical composition of a melt is a method long known to the art. The method is founded on the assumption that phase transformations occur at constant temperature and assumes that the solidification curve (i.e. the relationship between time and temperature during the process of solidification) prevents horizontal plateaux where growth of the solid phase takes place. These temperatures are read off on appropriate instruments, and a measurement of the composition of the melt is obtained from an equilibrium-phase diagram. The method is suited for analysing binary alloy systems, although some success has also been had in correcting obtained measuring values for the influence of a third element.

A close study of the solidification process, however, shows that the solid phase formed in a melt does not grow at a constant temperature unless the heat transport from the melt is infinitely slow. New and important information concerning the nucleation and growth conditions of the solid phase can thus be obtained by measuring temperature changes in connection with phase transformation: since the whole solidification process takes place within the source of a few minutes. To enable such changes to be measured, however, the solidification process must take place under certain conditions specified below.

The specified conditions are:

(1) the rate of transfer of heat from the test vessel is controlled;

(2) the initial temperature of the melt is above the nucleation temperature of the melt;

(3) convection in the melt during the solidification is substantially absent;

(4) dissipation of heat from the test vessel takes place in all directions during the solidification so that crystals formed on the walls of the test vessel fully encapsulate a residual melt disposed centrally of the mould;

(5) the temperature is measured by means of a temperature sensing device positioned centrally of the mould; and

(6) the material of the test vessel is inert

to the melt and cannot act as a nucleant for the melt.

With reference to condition (3), convection may be made substantially absent by magnetic means. With reference to condition (5), the temperature sensing device may be thermocouple.

If the above conditions are fulfilled and a solidification curve is thus recorded, the information given by the curve is such that it is possible to establish within a very short time, either manually or automatically, whether the measured value deviates from the desired values, and to correct any deviation which might be discovered. Deviations from desired values can, of course, be corrected by any known means, such as the addition of known grain refining substances, or by decanting or filtering surplus quantities of grain refining substances from the melt.

The conditions for assessing the recorded measurement values will now be discussed with reference to the accompanying drawings, in which Figures 1—3 illustrate the first portion of a solidification curve measured on pure aluminium having different nucleation properties and presenting single-phase crystal growth. Figures 4 and 5 illustrate a corresponding portion of a solidification curve showing the multi-phase crystal growth and Figure 6 illustrates multi-phase crystal growth with the solidification of cast iron the irregularities in the curve being obtained as a result of different types of multi-phase crystal growth.

1. Primary or single phase crystal growth with different quantities of nucleants

The first section of a solidification curve measured in accordance with the aforementioned conditions obtains for a melt of pure aluminium having a commercial purity (Al 99.7%) the principle course illustrated in Figure 1.

The reason for the increase in temperature during the so-called plateau phase is to be found in the fact that the growth rate of the crystals decreases from the surface of the sample mould in towards the centre and that the growth temperature is consequently increased. The test was carried out in a ceramic crucible having a volumetric capacity of approximately 40 cm³ and in the centre of which was placed a thermocouple. Prior to recording the desired information, the test vessel was completely submerged in molten pure aluminium and filled with a portion of the melt, at the same time obtaining the temperature of the melt.

The structure of pure aluminium corresponding to Figure 1 is almost completely formed of a few, long columnar crystals extending from the periphery in towards the centre of the sample. The solid phase has thus only nucleated at the walls of the mould at a

degree of under-cooling which is corresponded in Figure 1 by the value ΔT_1 .

Figure 2 illustrates a solidification curve drawn on the same base metal as that of Figure 1, but with the addition of effective nucleating particles.

The remarkable differences between the two solidification curves reside firstly in the value of the requisite degree of undercooling (ΔT_1) for the nucleation and secondly in the slope of the plateau.

When the nucleant is really effective, the required degree of undercooling will be small, since nuclei are formed throughout the whole sample. A network of solid phases is developed very early in this process and creates solid contact between the thermocouple and the walls of the test vessel. This dendritic network obtains a purer composition than the remainder of the melt and during the subsequent solidification process more enriched phases will solidify in the inter-dendritic regions. Subsequent to the residual melt having been enriched in this manner, the growth temperature will constantly decrease (micro-segregation effect).

Figure 3 illustrates a solidification curve for pure aluminium to which nucleating agents have been added in an insufficient quantity or which provide an insufficient effect.

The original degree of undercooling (ΔT_1) is, in this instance, greater than in the former instance. Moreover, the plateau has a slight upward inclination. This indicates that the formed nuclei have been unable to form a continuous network throughout the volume of the sample, but that the growth, as in Figure 1, is controlled by the growth of dendrites from the surface of the mould in towards the centre thereof.

It will be apparent from the foregoing that effective nucleation with primary crystal growth is characterized by a negative value on the temperature/time derivative ($dT/dr < 0$) during the plateau phase, i.e. that the curve during the plateau phase shows a falling temperature. It is also evident that the undercooling becomes smaller the more effective the crystal formation is.

2. Secondary or multi-phase crystal growth

To illustrate the conditions with secondary crystal growth, Figures 4 and 5 show solidification curves of an unmodified and a modified hypoeutectic aluminium-silicon cast alloy, the derivative dT/dr for these solidification curves also being shown.

Formation of the primary α_{Al} -phase is analogous with the foregoing description of the primary crystal growth. Of interest in Figures 4 and 5 is the temperature sequence with the secondary phase formation. In Al-Si-casting alloys, the eutectic reaction comprises a coupled growth of silicon and aluminium

phase, which influences the total eutectic growth rate.

A strong undercooling (ΔT_2) and a slow increase in the eutectic growth temperature (recalcescence) is the result. It has been found that the area under the derivative solidification curve or the time from the beginning of the nucleation period to the complete recalcescence provides a quantitative measurement which corresponds to the structure.

By adding different substances to the melt (for example sodium it is possible to stimulate nucleation of the silicon phase, and therewith also the growth conditions for the eutectic phases. This results in a lower degree of undercooling and a more rapid recalcescence, i.e. the area under the derivative and the time for recalcescence become small in comparison with the condition of unmodified material.

Multi-phase crystal growth with the secondary phase in different crystal forms

To illustrate the utility of the method for assessing secondary properties. Figure 6 illustrates a curve for the solidification of cast iron. The curve has, in principle, the same course as the previous curves based on aluminium and aluminium alloys. At the beginning of the solidification of the eutectic phase there is obtained in the solidification curve an inflection point which manifests itself as a maximum on the derivative. It has been found that the area of this peak is directly related to the quantity of graphite which is precipitated as flaky crystals, the subsequent undercooling and recalcescence disclosing the nodular graphite precipitation. Thus, the method of the present invention is extremely useful in assessing and regulating the precipitation of graphite in cast iron.

The test is carried out in a test vessel which fulfills given previously mentioned conditions on the rate of heat transfer from the sample, the temperature of the test vessel at the beginning of the measuring process, the convections in the melt, the geometric shape of the test cavity and the inertness of the walls of the test vessel with regard to nucleation. The metal from which the test vessel is made is determined by the nature of the metal melt to be tested. When measuring the crystal formation conditions in an aluminium melt, graphite crucibles can be used to advantage, while measurements made on cast iron require ceramic crucibles.

The volume of test material can vary within wide limits, but should suitably lie between 5—50 cm³ and the temperature should be measured at preferably not less than 1 cm from the walls of the test vessel.

The aforescribed equipment for sampling metal melts should suitably be provided with recording instruments (suitably a highly sensitive 2-channel tracing device, means for suppressing zero point, and derivating and

integrating devices) for measuring and recording:

1. Undercooling prior to primary nucleation
2. "the average plateau temperature" for chemical analysis of the melt
3. the slope of plateaux in the solidification curve, i.e. the derivative dT/dr
4. secondary undercooling and delayed recalescence, optionally with the assistance of a derivative and/or integrator unit.

One of the advantages afforded by the derivation process is that the derivator can be easily set to zero in the middle of the measuring area of the recording instrument. Possible drift in the thermocouple or changes in content areas for different materials do not therefore affect the position of the signal along the recording scale.

WHAT I CLAIM IS:—

1. A method of checking and adjusting the content of crystallization nuclei in a first melt comprising;

(a) taking a sample from the melt by immersing a test vessel in the melt;

- (b) removing the test vessel from the melt;
- (c) permitting the sample to solidify in the test vessel under certain conditions as hereinbefore specified;

(d) measuring the temperature of the sample at various times during the solidification of the sample;

(e) obtaining a first solidification curve by plotting a graph of temperature of the sample against time;

- (f) comparing at least one of the following characteristics of the curve; the slope of the primary plateau temperature and the area under positive values of the derivative of the curve with the corresponding characteristic(s) of a second solidification curve obtained by (i) measuring the temperature of a second melt at various times during solidification under said certain conditions, the second melt having the same composition as the first melt but having a desired content of crystallization nuclei and (ii) plotting a graph of the temperature of the melt against time; and

(g) adjusting the content of crystallization nuclei in said first melt if said compared characteristics differ substantially to make the content of crystallization nuclei in said first

melt substantially equal to said desired content.

2. A method according to Claim 1, wherein the temperature of the test vessel at the beginning of step (b) is substantially the same as that of the melt, the sample is permitted to solidify in the test vessel in step (b) under substantially convection free conditions and the test vessel is cooled at a regulated rate reproducible from test to test during solidification of the melt for a period of time of between 5 seconds and 5 minutes.

3. A method according to Claim 2, wherein the sample is taken in a quantity of from 5 to 50 cm³ and that the temperature is measured centrally of the sample at a distance of at least 1 cm from the walls of the test vessel by means of a thermocouple.

4. A method according to Claim 2 or 3, wherein convection in the test vessel is arrested magnetically.

5. A method according to any preceding claims, wherein the first melt is such that single-phase crystal growth occurs during its solidification and the characteristics of the curves which are compared are the primary plateau temperatures of the curves.

6. A method according to any of Claims 1 to 4 wherein the first melt is such that multiphase crystal growth occurs during its solidification and the characteristics of the curves which are compared are the areas under the positive values of the derivatives of the solidification curves.

7. A method according to any of claims 1 to 4, wherein the first melt is such that nodular iron forms during its solidification and the characteristics of the curves which are compared are the areas under positive values of the derivatives of the curves, which positive values correspond to solidification of flaky graphite crystals, the crystallization nuclei, the content of which may be adjusted in step (f), being crystallization nuclei for flaky graphite.

8. A method as claimed in Claim 1, substantially as described herein with reference to the accompanying drawings.

9. A material solidified from a melt, the content of crystallization nuclei in which have been checked and adjusted by a method as claimed in any preceding claim.

MARKS & CLERK.

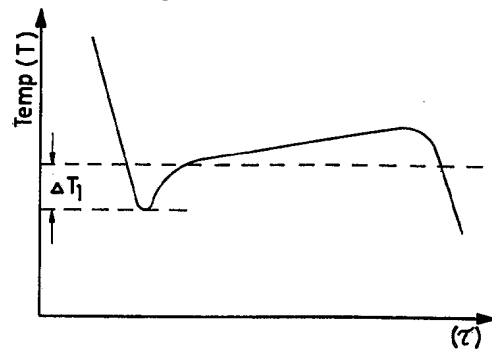


Fig. 1

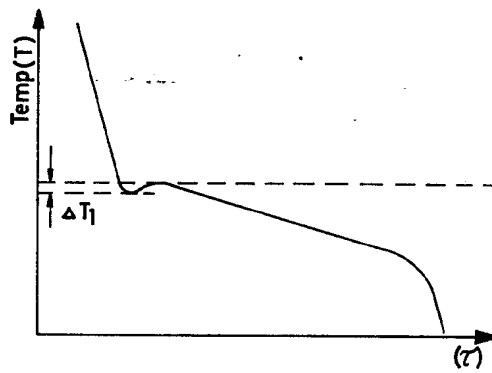


Fig. 2

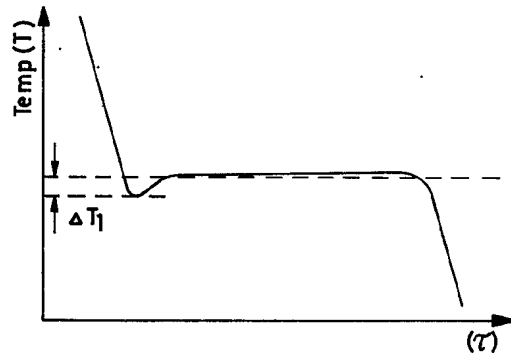
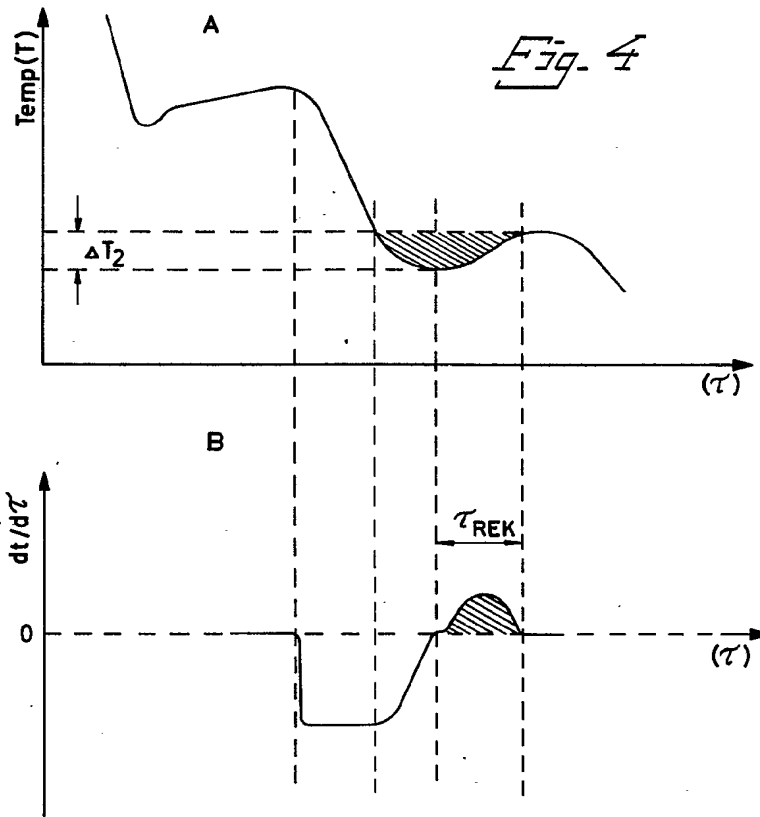


Fig. 3



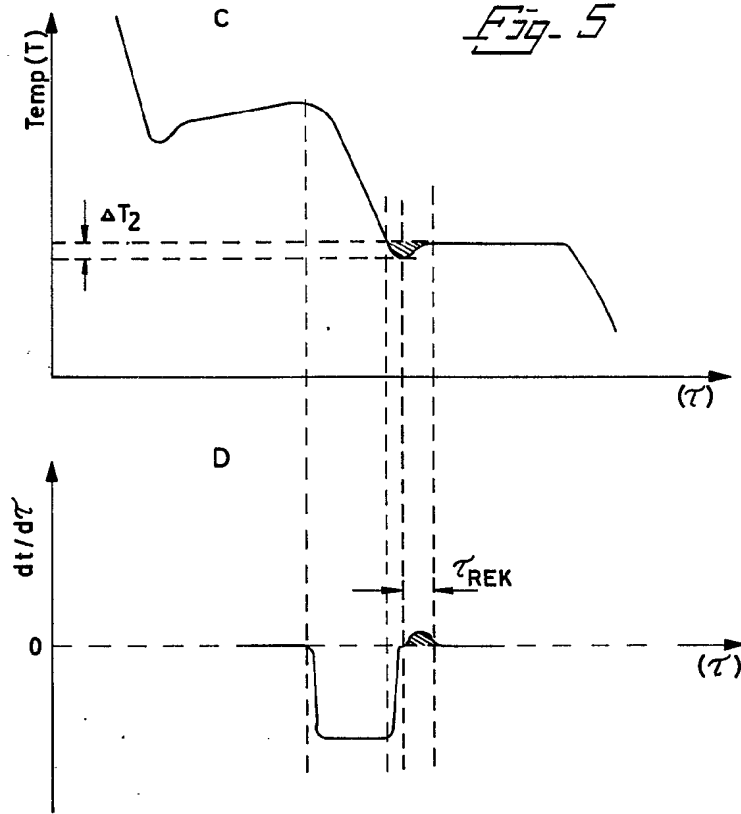
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COMPLETE SPECIFICATION

4 SHEETS

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the Original on a reduced scale

Sheet 3



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